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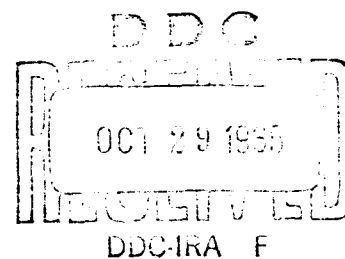
AFML-TR-65-2
Part I, Volume IV.

TERNARY PHASE EQUILIBRIA IN TRANSITION METAL-
BORON-CARBON-SILICON SYSTEMS

Part I. Related Binary Systems
Volume IV. Hf-C System

E. Rudy

Aerojet-General Corporation

TECHNICAL REPORT NO. AFML-TR-65-2, Part I, Volume IV

September 1965

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23 Sept. 1965

Subject: Report AFML-TR-65-2
Part 1, Volume IV
Ternary Phase Equilibria In Transition
Metal-Boron-Carbon-Silicon Systems

To: Research and Technology Division (MAMC)
Wright-Patterson Air Force Base, Ohio

Attn: Capt. R. A. Peterson

Inclosure (1) is submitted in partial fulfillment of Contract AF 33(615)-1249.

AEROJET-GENERAL CORPORATION

R. L. Fulford, Supervisor
Editorial Services
Technical Publications

Incl: (1) Copies 1 through 18, Report AFML-TR-65-2, Part 1, Vol. IV

TERNARY PHASE EQUILIBRIA IN TRANSITION METAL-BORON-CARBON-SILICON SYSTEMS

Part I. Related Binary Systems
Volume IV. Hf-C-System

E. Rudy

FOREWORD

The work described in this report has been carried out at the
Materials Research Laboratory, Aerojet-General Corporation,
Sacramento, California, under USAF Contract No. AF 33(615)-1249.
The contract was initiated under Project No. 7350, Task No. 735001,
and was administered under the direction of the Air Force Materials
Laboratory, Research and Technology Division, with Captain R.A. Peterson
acting as Project Engineer, and Dr. E. Rudy, Aerojet-General Corporation,
as Principal Investigator. Professor Dr. Hans Nowotny, University of
Vienna, served as consultant to the project.

The project, which includes the experimental and theoretical in-
vestigation of selected ternary systems in the system classes Me_1-Me_2-C,
$Me-B-C$, Me_1-Me_2-B, $Me-Si-B$, and $Me-Si-C$, was initiated on
1 January 1964. The investigation of selected binary metal-carbon and
metal-boron systems was performed as a subtask to the work on the ternary
diagrams.

The author wishes to acknowledge the experimental help received
from D. P. Harmon, C. E. Brukl, and St. Windisch. Of further assistance
were: J. Pomodoro (sample preparation), J. Hoffman (metallographic
preparations), and R. Cobb (X-ray exposures). The chemical analytical
work was carried out under the supervision of Mr. W. E. Trahan, Quality
Control Division. The drawings were prepared by R. Cristoni and
Mrs. J. Weidner typed the report.

The manuscript of this report was released by the author July 1965
for publication as an RTD Technical Report.

Other reports issued under USAF Contract AF 33(615)-1249 have included:

Part I. Related Binaries

Volume I. Mo-C System

Volume II. Ti-C and Zr-C System

Volume III. Mo-B and W-B Systems

Part II. Ternary Systems

Volume I. Ta-Hf-C System

Volume II. Ti-Ta-C System

Part III. Special Experimental Techniques

Volume I. High Temperature Differential Thermal
Analysis

Part IV. Thermochemical Calculations

Volume I. Thermodynamic Properties of Group IV, V,
and VI Binary Transition Metal Carbides.

T   ical report has been reviewed and is approved.

W. G. RAMKE
Chief, Ceramics and Graphite Branch
Materials and Ceramics Division
Air Force Materials Laboratory

ABSTRACT

The alloy system hafnium-carbon was investigated by means of X-ray, DTA, and melting point techniques on chemically analyzed alloys, and a complete phase diagram was established.

The results are discussed and compared with previously reported data.

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I. INTRODUCTION AND SUMMARY

A. INTRODUCTION

The present report is one in the series of documentary reports on the phase relationships in refractory binary carbide and boride systems. The initial task of this program, the establishment of the phase-relationships in ternary metal-carbon-boron-silicon systems, was re-directed in November 1964 to include also the partial or complete investigation of selected binary systems. The ultimate objective of this extended effort is to provide reliable boundary system data for the interpretation of the phase-relationships in the ternary systems.

Due to the limited time available for these investi-gations, not every detail in these systems could be examined as closely as probably would have been desirable. Nevertheless, it is felt, that the results reported should represent the phase-relationships in these systems to a sufficient degree of accuracy and provide valuable supplemental informa-tion to the existing data.

In every instance, care was exercised to obtain reliable results. Wherever possible, independent methods of investigation were used to countercheck the experimental findings.

B. SUMMARY

Based on the results obtained from X-ray, metallographical, and differential-thermoanalytical investigations on chemically analyzed alloys, a constitution diagram for the binary system hafnium-carbon was established (Figure 1, and Table i).

1
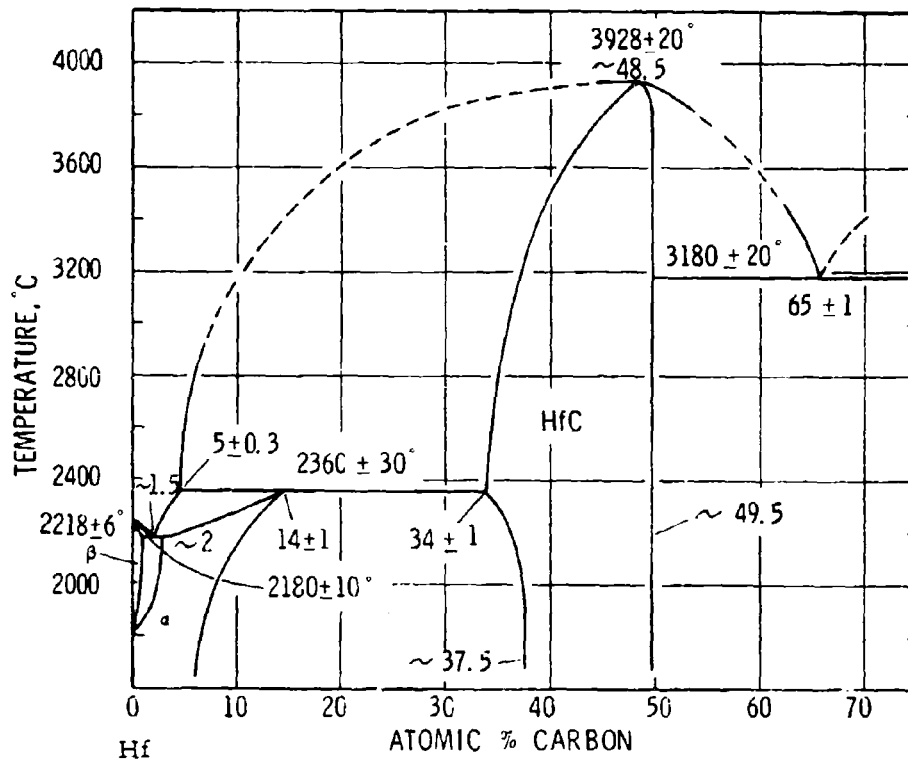
Figure 1. Phase Diagram of the System Hafnium-Carbon

[The Temperature Uncertainties Refer to the Precision
of the Measurements and do not include the Calibration
Errors (Section III-3)]

1.   The Hafnium-Phase*

β-Hafnium melts at 2218 ± 6°C. The low tempera-

ture hexagonal close-packed (α) modification,transforms at 1795 ± 35°C

(extrapolated to 100% Hf) into the body centered cubic allotrope. Under

lattice dilatation, the α-modification takes up to 14 atomic % carbon into

---

*The starting material used for the investigations contained 4 At% zirconium.
 For the sake of clarity in the text, this starting material is referred to as
 "hafnium".

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Table 1: Reactions Isotherms in the System Hafnium-Carbon

Temperature °C	Reaction	Composition of the Equilibrium Phases, At% C			Type of Reaction
3928 $\pm$ 20°	L $\longleftrightarrow$ HfC$_{1-x}$	~48.5	~48.5	-	Congruent Trans.
3180 $\pm$ 20°	L $\longleftrightarrow$ HfC$_{1-x}$+C	65$\pm$1	~49.7	~100	Eutectic Reaction
2360 $\pm$ 30	L + HfC$_{1-x}$ $\longleftrightarrow$ α-ss	5$\pm$0.3	34$\pm$1	14$\pm$1	Peritectic Reaction
2218 $\pm$ 6	L $\longleftrightarrow$ β-Hf	-	-	-	Melting Point of Hafnium
2180 $\pm$ 10	L $\longleftrightarrow$ α + β	~1.5	<1	~2	Eutectic Reaction
1795 $\pm$ 35°	β $\longleftrightarrow$ α	-	-	-	α-β-Transformation in Hafnium

solid solution and is stabilized to higher temperatures. A eutectic at 2180 $\pm$ 10°C and ~1.5 At% carbon is formed between the α(<1 At% C) and the β(~2 At% C)-modification. The β-(Hf,C) solid solution forms in a peritectic reaction at 2360 $\pm$ 30°C from melt and monocarbide according to

$$P \ (5 \ At\% \ C) + B1 \ (34 \ At\% \ C) \longrightarrow \alpha\text{-}(Hf,C)\text{-}ss \ (14 \ At\% \ C)$$
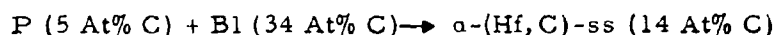
2.   Hafnium Monocarbide

Hafnium monocarbide, with a face centered cubic, B1-type of crystal structure extends at 1600°C from approximately 38 At% C (a = 4.619 Å) to ~49.5 At% C (a = 4.640 Å). At 2360°C, the low carbon boundary is located at ~34 At% C (a = 4.608 Å). The phase, which melts congruently at 3928 $\pm$ 20°C at a carbon concentration of 48.5 $\pm$ 0.5 At% C, forms a eutectic with graphite. The eutectic point is located at 3180 $\pm$ 20°C and 65 $\pm$ 1 At% C.

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II. LITERATURE REVIEW

Only one intermediate carbide phase occurs in the system. Hafnium monocarbide, with a face-centered cubic, B1-type of structure, was first prepared by K. Moers[1,2] and its structure was clarified by K. Becker[3]. The phase extends from 37 (a = 4.614 Å) to approximately 50 atomic percent carbon (a = 4.633 Å) at 1550°C[9,10]. The most probable lattice parameter for the stoichiometric composition is a = 4.640 Å (Table 2). For further references on earlier work, the data compilation in M. Hansen's "Constitution of Binary Alloys"[12], as well as in R. Kieffer and F. Benesovsky's "Hartstoffe"[13] may be consulted.

Conflicting results have been reported for the metal-rich portion of the hafnium-carbon system[8,9,16,18]. M.I. Copeland[16] has presented a diagram (Figure 2), where about equal solubilities in the α- and β-modification were reported. The peritectoid temperature decomposition of the α-(Hf, C) solid solution was placed at 1890°C. A radically different diagram was presented by R. G. Avarbe, et.al.[18] (Figure 3), indicating extended solid solution formation of the α-Hf-phase, and only a very nominal carbon solid solubility in the β-modification. The diagram presented by R. V. Sara and C. E. Lowell[8] follows closely the layout proposed by M. I. Copeland.

Reported melting temperatures for the monocarbide phase vary between 3820 and 3895°C (Table 3). The data obtained by the resistive-heating (containerless) method[ref. 14 and 15] are probably to be given preference, since interaction between test and container material in other techniques used may have lead to erroneous results[8]. The existence of a eutectic reaction isotherm between the monocarbide and graphite at temperatures
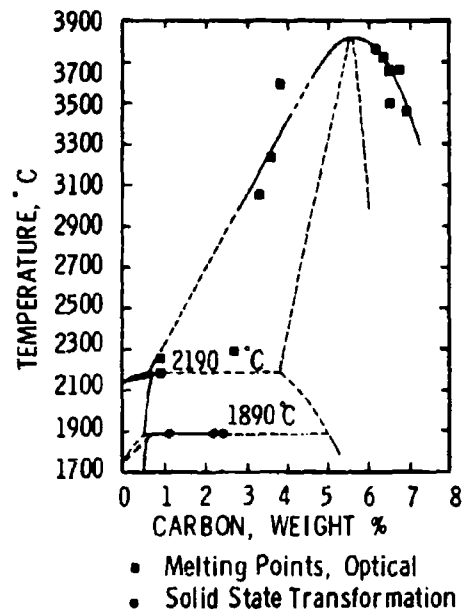
Figure 2. Hafnium-Carbon Phase Diagram
(M. I. Copeland, 1962)
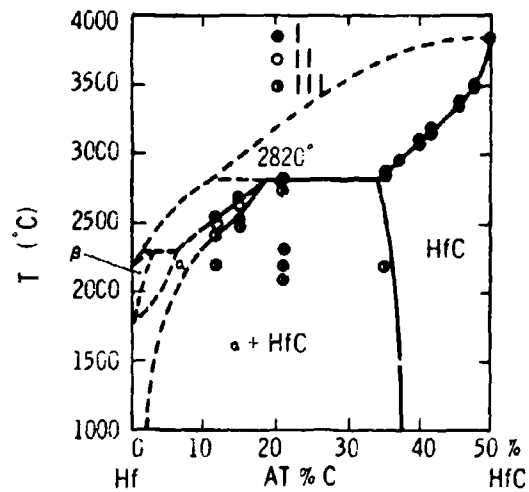
Figure 3. Hafnium-Carbon Phase Diagram
(R. G. Avarbe, et.al., 1962)

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Table 2. Reported Lattice Parameters for Hafnium Monocarbide

Composition, At% C	Lattice Parameter, $\overset{\circ}{A}$	Investigator	Ref.
50	4.646	Curtis, et.al., 1959	4
50	4.641	Cotter and Kohn, 1954	5
50	4.64	Glaser, et.al., 1953	6
47.2	4.6382 ± 0.0003	Krikorian, et.al., 1963[4]	31
49.2	4.643	Sara and Lowell, 1964	8
35	4.622	Sara and Lowell, 1964[5]	8
37	4.614	Benesovsky and Rudy, 1960	9
50	4.631	Benesovsky and Rudy, 1960[6]	9
50	4.637	Zhelankin and Kutsov, 1963[7]	11
36.7	4.607	Zhelankin and Kutsov, 1963[7]	11

Table 3. Maximum Melting Temperatures for
Hafnium Monocarbide (Literature Data)

Investigator	Ref	Melting Temperature, °C	Composition
Agte and Alterthum, 1930	14	3890 ± 150	$HfC_{\sim 1.0}$
Adams and Beall, 1963	15	3895°	$HfC_{0.985}$
Copeland, 1962	16	3820 ± 100	$HfC_{0.865}$
Sara and Lowell, 1964	8	3820-3820°	$HfC_{0.905}$

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in the vicinity of 3000°C is firmly established from previous work (Table 4).

Table 4: Literature Data for the HfC-C Eutectic Reaction Isotherm.

Investigator	Ref	Eutectic Temperature °C	Eutectic Composition At% C
Copeland, 1962	16	~3400	N.D.
Adams and Beall, 1963	15	~3220	< 68
Portnoi, et.al., 1961	17	3250 ± 500	~85
Cotter and Kohn, 1954	5	2800	N.D.
Krikorian, 1962	7	2915	N.D.
Sara and Lowell, 1964	8	3150	66

III.   EXPERIMENTAL PROGRAM

A.   STARTING MATERIALS

The experimental alloy material was prepared from sponge-hafnium, hafnium metal powder (Wah Chang Corporation, Albany, Oregon), and high purity graphite. The metal powder had the following impurities (contents in ppm): Al-20, C-210, Nb-680 (<1000)*, Cr-<20, Cu-40, Fe-265, H-55, Mo-40, N-200 (<300), O-810 (<1000), Si-<40 (10), Ta-<200 (400),

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*The concentration figures given in the brackets are data from a control analysis performed at the Analytical Chemistry Laboratory of Aerojet-General Corporation.

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Ti-20, W-235, sum of remainder-< 100; it further contained 4.1 At% zirconium. Lattice parameters of a = 3.19_6Å and c = 5.05_7 Å were obtained from a powder diffraction pattern with Cu-K_α radiation. This compares favorably with reported literature values of a = 3.194 - 3.199 Å, and c = 5.0510 - 5.0620 Å[1]. The sponge-hafnium had the following analysis (impurity contents in ppm): Al-94, Cu-<40, Fe-185, Cl-100, Mg-450, N-30, O-680, Si-<40, Ti-250, W-<2-. The zirconium content of the sponge was 4 At%.

To circumvent difficulties in the preparation of the alloys, arising from the violent reaction between hafnium and carbon to form the monocarbide, prealloyed hafnium monocarbide, prepared by direct combination of the elements in a high vacuum furnace (2 hrs at 1950°C, 5.10^{-6} Torr) was used. The reaction product, which had a total carbon content of 49.3 At% C (a = 4.640 Å), was comminuted in hard-metal lined ball mills to a grain size of <44 micrometers. Cobalt traces, which were picked up during ball-milling,were removed by leaching the powder in a 5 normal mixture of hydrochloric and sulfuric acid.

The spectrographic grade graphite powder (Union Carbide Corporation, Carbon Products Division) had the following analysis: Sum of metallic impurities (Al + Cu + Mg + Si + Fe) - 9 ppm, ash-<500 ppm, and 100 ppm volatile matter. No second phase impurities could be detected in strongly overexposed powder patterns. The lattice parameters, determined from an exposure with Cu-K_α radiation were a = 2.463 Å, c = 6.729 Å. These values are in good agreement with reported parameters of a = 2.461 Å and c = 6.708 Å[1].

B.   EXPERIMENTAL PROCEDURES

1.   Sample Preparation and Heat Treatment

Specimens were prepared for melting point, differential thermal analysis, as well as for X-ray and metallographic investigations. Alloys in the concentration range from 35 to 70 At% carbon were prepared by hot-pressing[2] the well-blended components in graphite sleeves at temperatures varying between 2200 and 2800°C. Excess metal-containing alloys were prepared by cold-pressing and subsequent sintering in a tungsten mesh element furnace (R. Brew Company) under a vacuum better than 2×10^{-6} Torr.

A number of alloys was also melted in a non-consumable electrode arc furnace (Model ZAK) under a high purity helium atmosphere and subjected to the same homogenization treatments. While this method produced satisfactory results with alloy compositions from within the homogeneous range of the monocarbide phase and also for alloys having excess graphite, considerable segregation of the alloy mixtures in excess metal-containing alloys was noticed. Somewhat better controllable and reproducible conditions were obtained by electron-beam melting: nevertheless, extended heat-treatment after the melting procedures were in both cases necessary in order to re-establish equilibrium. Based on these findings, samples for the metallographic studies were therefore prepared by equilibration of the prehomogenized alloy specimens at the desired temperature in the Pirani-furnace[2]. Rapid quenching was achieved by dropping the sample from the equilibrium temperature into a preheated tin bath.

The specimens for the differential-thermoanalytical investigations in the very metal-rich portion of the system (0-10 At% carbon)

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were prepared by repeated electron-beam melting of cold-compacted mixtures of hafnium and graphite powder, and subsequent machining of the small ingots into the required dimensions.

2. **Differential Thermal Analysis**

Apparative details of the DTA-setup have been described earlier[2, 3]. High purity graphite was used as container material. For the studies of the α-β-transformation of hafnium, the sample proper was physically insulated from the container walls by a loose stuffing (~1 mm) of hafnium powder, in order to retard interaction of the specimen surface with graphite. No disadvantageous interference was encountered in the investigations within the solidus range; however, carburization was comparatively fast at temperatures close to or above melting.

3. **Melting Points**

The melting temperatures of the alloys were determined with the Pirani-technique. Apparative details of the furnace, which was designed and built in this laboratory, were described earlier[30].

Excess metal-phase containing alloys were melted under vacuum. To prevent carbon and hafnium losses from the alloys in the high melting monocarbide region, the furnace chamber was pressurized to 2 1/4 atmospheres with high purity helium, after the alloys had received a final degassing treatment at temperatures between 2200 and 2550°C. The temperature measurements were carried out with a disappearing-filament type micropyrometer, which was calibrated against certified standard lamps and a standard pyrometer from the National Bureau of Standards. The overall temperature uncertainties are ± 10°C at 2300°C, ~ ± 17°C at 3000°C, and ± 30°C (estimated) at 4000°C. The

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temperature uncertainties referred to in the text denote the precision of the measurements, and do not include calibration errors. The overall uncertainties in the melting temperatures can be computed from

$$\bar{\sigma}_m = \pm\sqrt{\sigma_c^2 + \sigma_m^2}$$

where $\bar{\sigma}_m$ stands for the overall temperature uncertainty, σ_c for the average calibration error, and σ_m denotes the precision of the measurement.

4. X-Ray Analysis

Since the crystal structures of all phases were known, only powder patterns (Cu-K_α-radiation) were prepared.

The exposures were taken in a 57.4 mm dia. camera on a Siemens-Crystalloflex II unit and the film readings were taken on a Siemens-Kirem coincidence scale. The precision micrometer allows the measurements to be accurate to $\pm$ .01 mm. Use of two-radian (114.6 mm dia) cameras was not considered, since the accuracy of the lattice spacings obtainable with the small camera are well within the accuracy limits set by the uncertainties in the chemical analysis.

5. Metallography

For the metallographic examination of the alloys, the specimens were mounted in an electrically conductive mixture of copper-coated lucite powder and diallylphtalate. The mounted specimens were coarse-ground on silicon-carbide papers with grit sizes varying between 120 and 600. They were polished on nylon-cloth, using a slurry of 0.05 micron alumina in a 10 percent oxalic acid solution. The etching procedures varied with the carbon content of the alloys. Good results were obtained with the mixtures described in Table 5.

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Table 5: Etching Procedures for Hafnium-Carbon Alloys

Alloy, At% C	Etching Solution (percent base solution* in water)	Dip-etch, time
0-25	1	1 sec
26-35	10	to
36-55	100	3 min
56-70	—	no etching required

*Base Solution: 4 parts aqua regia plus 1 part HF

6. Chemical Analysis

The majority of the alloys were analyzed for their carbon content, using the standard combustion technique. The oxygen content of selected specimens was determined by gas fusion analysis. The results were not as consistent as the carbon analysis, and sometimes variations up to $\pm$ 400 ppm were noticed; in neither case, however, were higher values than 600 ppm found.

C. RESULTS

1. Hafnium

The melting point of hafnium was determined on as- pressed as well as pressed and high-vacuum sintered ($<10^{-5}$ Torr specimens); a value of 2218 $\pm$ 6°C was derived from four measurements.

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2. α-β-Transformation of Hafnium

The experimental alloy material for these investigations was prepared by remelting the sponge-hafnium several times in an electron-beam furnace (Heraeus ES 2/4), until no gas evolution could be observed. The resulting bars were then fabricated into samples of desired size (~ 14 mm x 16 mm high), and subjected to the DTA-studies. The DTA-runs were performed under vacuum as well as under a high purity helium atmosphere. The results were identical.

A slight difference between the reaction onset on the heating and cooling cycle of the runs was noticed in all experiments (Figure 4, Table 6). This may be indicative, that despite repeated electron-beam melting, some traces of interstitial elements may have remained in the metal. In view of the extreme negative partial free energy of oxygen at low concentrations, this is not surprising (the concentration remains constant, if $\dot{n}_o > \dot{n}_{Hf}$, the molar vaporization rates of oxygen and hafnium are equal at a given temperature).

In order to achieve more effective desoxydation conditions, small amounts of boron were added to the hafnium prior to the electron-beam melting in a further experiment. This resulted in somewhat lower transformation temperatures (Table 6). A post-experiment analysis performed on one of the alloys showed a drop of the zirconium content from 4 At% in the original raw material to 1.9 ± 0.5 At% after melting. Applying the corrections suggested by D. K. Deardorff and H. Kato[19], and taking into account the temperature uncertainties of the pyrometer readings, a value of $1795 \pm 35 °C$ is derived for the temperature of the α-β-transformation in pure hafnium.

13
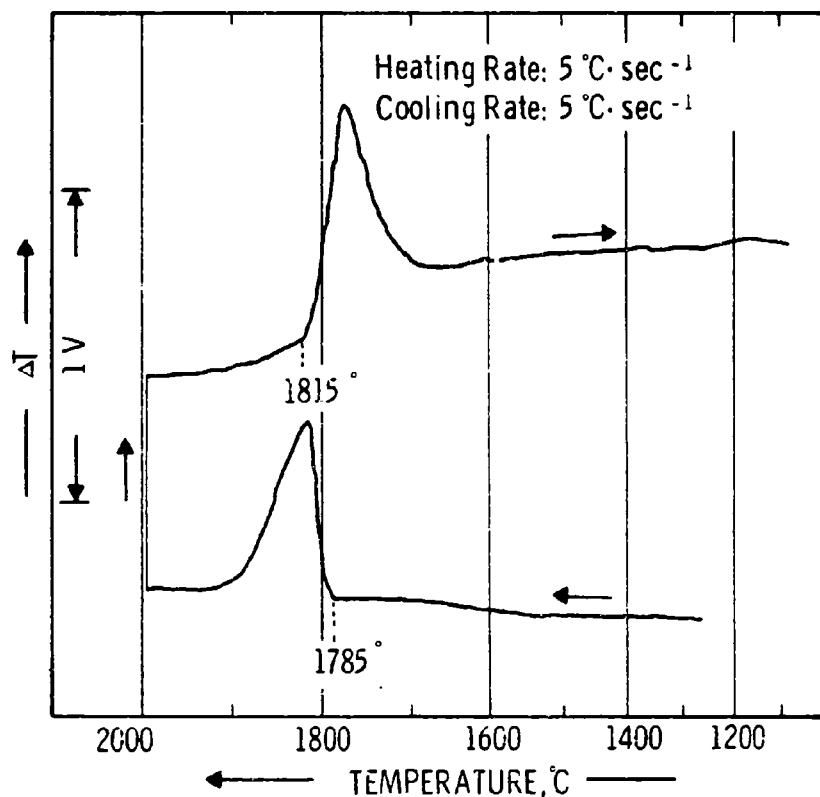
Figure 4. DTA-Thermogram of Hafnium

Alloy Material: Hf-Sponge (4 At% Zr, <0.4 At% O),
Remolten Twice in an Electron-Beam
Furnace. Zr-Content After Melting:
~1.9 At%.

This value agrees very well with the determination
by D. K. Deardorff and H. Kato[20] (1760 ± 35°C), but less favorably
with more recent determinations by A. Taylor and N.J. Doyle[21] and
R. G. Ross and W. Hume-Rothery[22] (Table 7).

The cause for the relatively large differences among
the various investigators may possibly be sought in varying interstitial
impurity contents of the starting materials as well as the apparative
techniques used for the determinations.

Table 6. Temperatures for the α-β-Transformation in Hafnium
Obtained by Differential Thermal Analysis

Sample	Thermal Arrests (Mean Temperatures) °C		
	Heating Cycle	Cooling Cycle	Average
1	1785	1815	1800+25
2	1795	1805	1800+25
3*	1775	1810	1790+25
4**	1770	1780	1775+25

Legend to Table 6:

* Zr-content after electron-beam melting
1.9 + 0.5 At%

** 1 At% Boron added prior to electron-beam
melting.

3. Effect of Carbon on the α-β-Transformation in
Hafnium

The experimental studies were carried out using the
same starting materials as described under paragraph 2 of this section.

In order to delineate the features in the low-carbon
portion of the system, a hafnium specimen was repeatedly heated and
equilibrated in a graphite holder in the DTA-apparatus, and differential-
heating and cooling studies were performed after each equilibration experi-
ment.

The heating curves are shown in Figure 5. With
increasing carbon pick-up, the onset of the α-β-phase reaction is gradually
shifted towards higher temperatures and, after sixteen runs, has almost
disappeared. The carbon concentration of the alloy obtained by a subsequent

Table 7: Reported Temperatures for the α-β-Transformation in Hafnium*

Author	Ref.	Transf.Temp. °C	Remarks
Zwikker, 1926	23	1327 to 1527	--
Duwez, 1951	24	1310°	--
Fast, 1952	25	1950°	extrapolated to 100% Hf
Taylor & Doyle, 1960, 1964	21	1950°	4.41 At% Zr
Grant & Giessen, 1960	26	1840°	4.41 At% Zr
Ross & Hume-Rothery, 1963	22	1995 ± 70°	extrapolated to 100% Hf
N.H.Krikorian, 1963	27	1750 ± 20°	--
D.K. Deardorff & H. Kato, 1958	20	1760 ± 35°	extrapolated to 100% Hf
Present Investigation	-	1795 ± 35°	extrapolated to 100% Hf

*In the meantime a publication by P. A. Romans, O. G. Pasche, and H. Kato (J. Less Common Metals 8 (1965), 213) became available. They report a transformation temperature of 1770°C for pure hafnium.
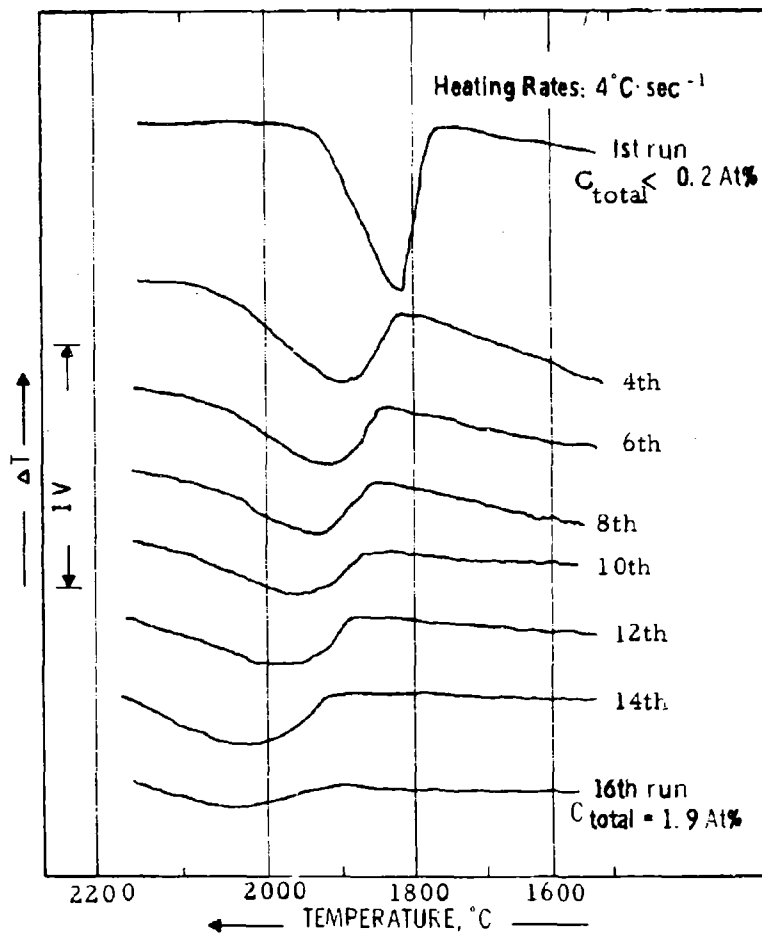
Figure 5. DTA-Thermograms (Heating) of Hafnium After
Repeated Exposure to Graphite

(Note: The alloy was equilibrated for 1 minute at
2160°C prior to each subsequent run)

chemical analysis was 1.9 At%. In DTA-runs performed on alloys

with carbon concentrations of 3, 5, 10, and 15 At% C, no deviations from

the normal course of the base line, which could be related to heat-effects

associated with the α-β-phase reaction, were detected.

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Cooling Rates: 4 °C· sec^{-1}

$C_{total} < 0.2$ At%

1st run

3rd

5th

7th

9th

11th

16th run

$C_{total} = 1.9$ At%

$\Delta T \longrightarrow$ 1 V

2200   2000   1800   1600   1400   1200
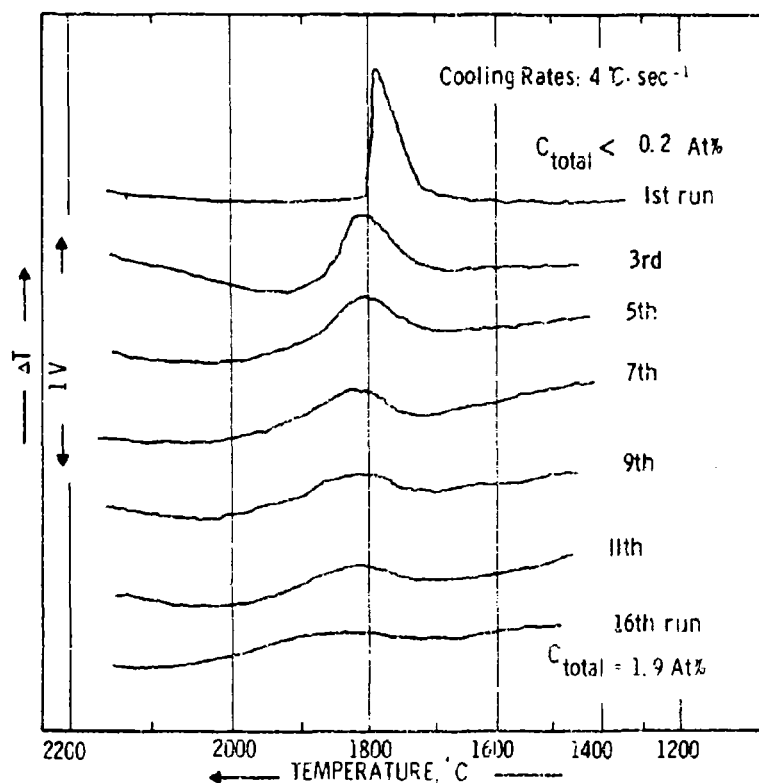
$\longleftarrow$ TEMPERATURE, °C

Figure 6. DTA-Thermograms (Cooling) of Hafnium After
Repeated Exposure to Graphite.

(Note: The alloy was held for 1 minute at 2160°C prior
to each subsequent run)

A similar trend of the (bivariant) reaction tempera-
tures is observed in the corresponding thermograms obtained on the cool-
ing cycle (Figure 6). The relatively wide temperature gap between the
heating and cooling cycle is further indicative of the steep increase of the tem-
perature range of the transformation reaction upon small carbon additions.

In order to differentiate between the various reaction
types possible in the very metal-rich region of the system (c.f. peritectic

18
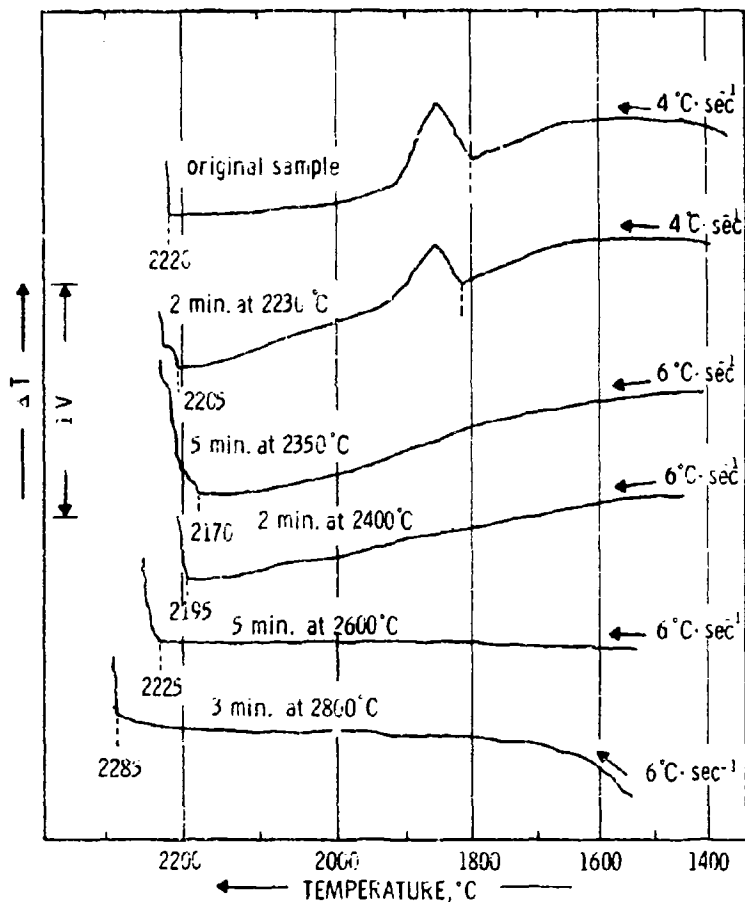
Figure 7: DTA-Thermograms (Heating) of Hafnium in
Contact with Graphite.

(The time and temperature figures indicated on
each curve refer to the equilibration treatment
in the previous run).

decomposition of the β-modification; possible formation of a eutectic

between the α- and β-modification) a series of analogous experiments

as described before, but with the temperature range of the runs extended

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to the liquidus region, were performed. The results (Figure 7) are clearly in favor of a eutectic type of reaction. The existence of a eutectic reaction isotherm was also independently verified by melting point determinations on low-carbon alloys, (Figure 8 and Table 6).

Figure 8. Melting Temperatures of Hafnium-Carbon Alloys

Metallographic examination of low carbon alloys revealed evidence of the α-β-transformation only in alloys with less than three atomic percent carbon (Figure 9), whereas at higher carbon-concentrations only the α-phase is observed (Figure 10).

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Table 8: Melting Temperatures of Hafnium-Carbon Alloys

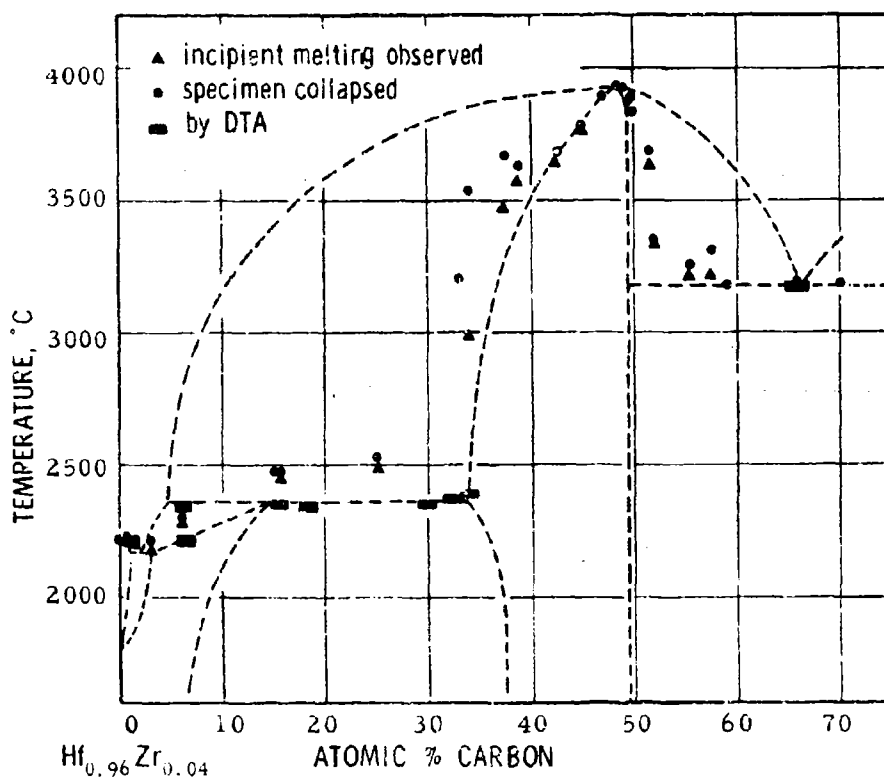| No	At% C Nominal	At% C Anal.	Melting Temperatures °C Incipient	Melting Temperatures °C Collapse	Phases Present After Melting (X-Ray)	Melting
1	1	1.2	2200	2230	n.d.	heterogeneous
2	2	n.d.	2199	2219	n.d.	fairly sharp
3	3	3.4	2180	2195	Hf-ss	fairly sharp
4	6	n.d.	2195	2290	Hf-ss	heterogeneous
5	6.5	6.6	2280	2290	Hf-ss	very heterog.
6	10	n.d.	2390	2460	B1 + Hf-ss	very heterog.
7	15	n.d.	2420	2470	B1 + Hf-ss	very heterog.
8	25	n.d.	2487	2525	B1 + Hf-ss	very heterog.
9	30	30.7	2470	2680	B1 + Hf-ss	very heterog.
10	32	33.2	2370	3204	B1 + trace Hf-ss	very heterog.
11	35	33.9	2981	3540	B1 + trace Hf-ss	very heterog.
12	39	37.5	3467	3675	B1	very heterog.
13	41	38.8	3578	3635	B1	very heterog.
14	44	42.6	3644	3675	B1	heterogeneous
15	47	45.3	3770	3790	B1	heterogeneous
16	47	47.2	3896	3896	B1	fairly sharp
17	49	48.5	3928	3928	B1	sharp
18	49	48.6	3921	3921	B1	sharp
19	50	49.2	3886	3886	B1	sharp
20	51	49.8	3874	3874	B1	sharp
21	51	49.9	3827	3827	B1	fairly sharp
22	53	51.60	3630	3686	B1	very heterog.
23	55	52.40	3344	3344*	B1	very heterog.
24	56	53.0	3300	3350*	B1 + C	very heterog.
25	57	56.1	3210	3260	B1 + C	slight. heterog.
26	60	57.6	3214	3300	B1 + C	heterog.
27	60	58.5	3180	3180	B1 + C	slight heterog.
28	63	-	3195	3195	B1 + C	slight. heterog.
29	66	65.2	3177	3177	B1 + C	sharp
30	68	66.7	3183	3183	B1 + C	sharp
31	70	68.0	3188	3188	B1 + C	sharp
32	74	73.2	3193	3193	B1 + C	fairly sharp

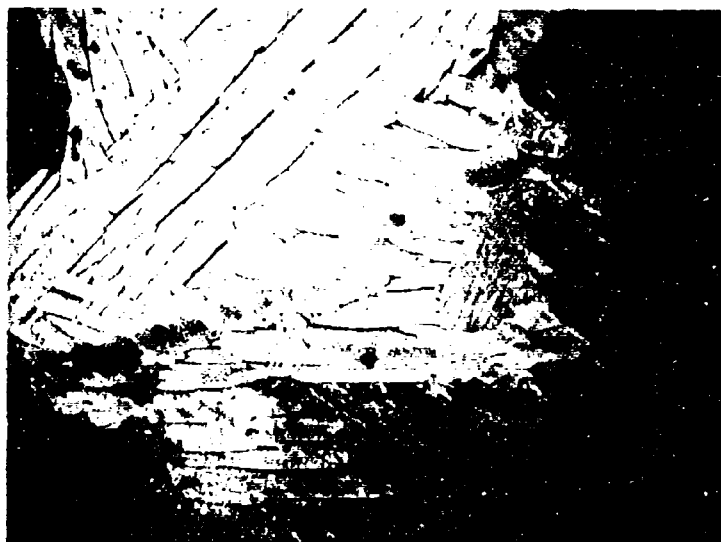Legend to Table 8: *Samples sag gradually without detectable appearance of melt.

Figure 9. Hf-C (1.2 At% C), Rapidly Quenched from 2220°C. X500
β-Hf (Transformed) with Traces of α-Hf.

Figure 10. Hf-C (3.4 At% C), Rapidly Cooled from 2195°C. X250
α-(Hf,C) Solid Solution

4. The Concentration Range from 5 to 34 At% C

Melting of the alloys in this concentration range occurs extremely heterogeneously (Table 8), and incipient melting was very difficult to recognize; sample deformation, or any sign of melting usually could not be observed below approximately 2500°C. Due to this behavior, the melting temperatures of the alloys as determined by the DTA-technique (Figure 8) are therefore more accurate than the data obtained by the Pirani-method.

DTA-runs performed on electron-beam melted as well as hot-pressed and sintered samples (Figures 11 through 15) revealed an average equilibrium temperature for the peritectic reaction

$$P + B1 \longrightarrow \alpha\text{-Hf-ss}$$
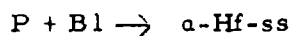
of $2360 \pm 30°C$. The peritectic reaction at 2360°C can still be traced in alloys with 30 and 33 atomic percent carbon, as evidenced by the slight endotherms on the corresponding DTA-thermograms in Figures 14 and 15. However, the incipient melting temperatures rise rapidly, as the carbon concentration exceeds 34 atomic percent (Figure 16).

Metallographic analysis was performed on a large portion of the sample material in order to obtain independent confirmation of the results. Arc melting with subsequent equilibration treatment at the desired temperature as a method for preparing the sample material was discarded, since physical separation (floating) of the carbide on the metal-melt occurred, and no defined alloy material could be prepared. In view of these difficulties, the alloys for the metallographic examinations were

23
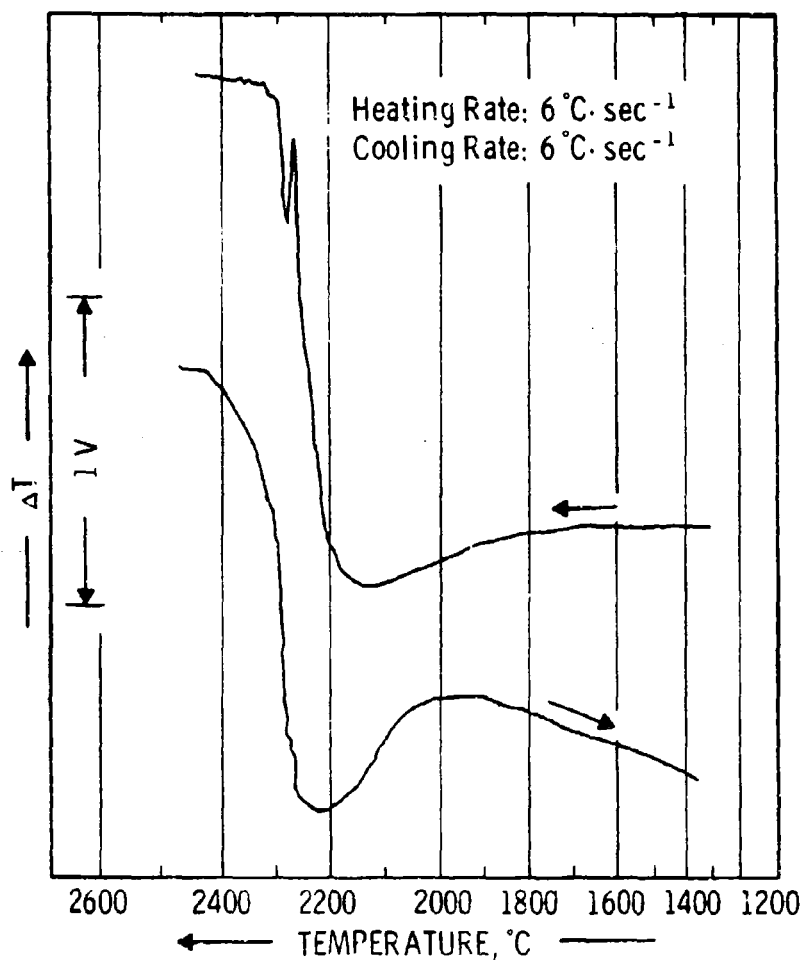
Figure 11. DTA-Thermogram of a Hf-C Alloy with 6 Atomic Percent Carbon,

prepared by melting and subsequent equilibration of the prehomogenized alloys in the Pirani-furnace. Following this procedure, well-defined alloy material was obtained, yielding consistent results.

Figure 12. DTA-Thermogram of a Hf-C Alloy with
15 Atomic Percent Carbon.

Figure 13. DTA-Thermogram of a Hf-C Alloy with
18 Atomic Percent Carbon.
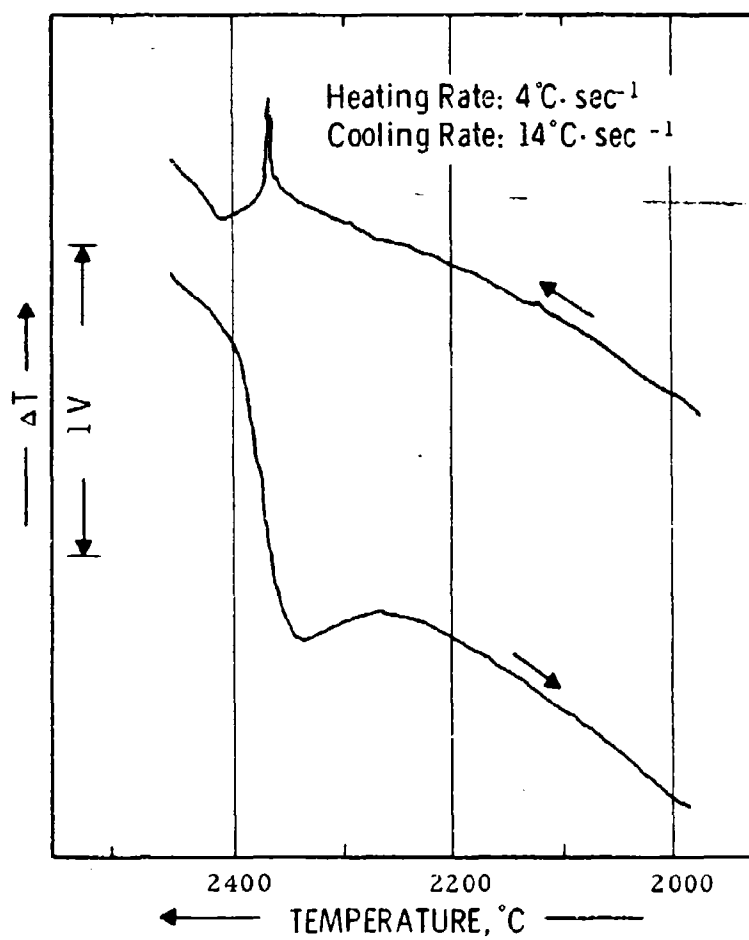
Figure 14. DTA-Thermogram of a Hf-C Alloy with 30 Atomic Percent Carbon.

26
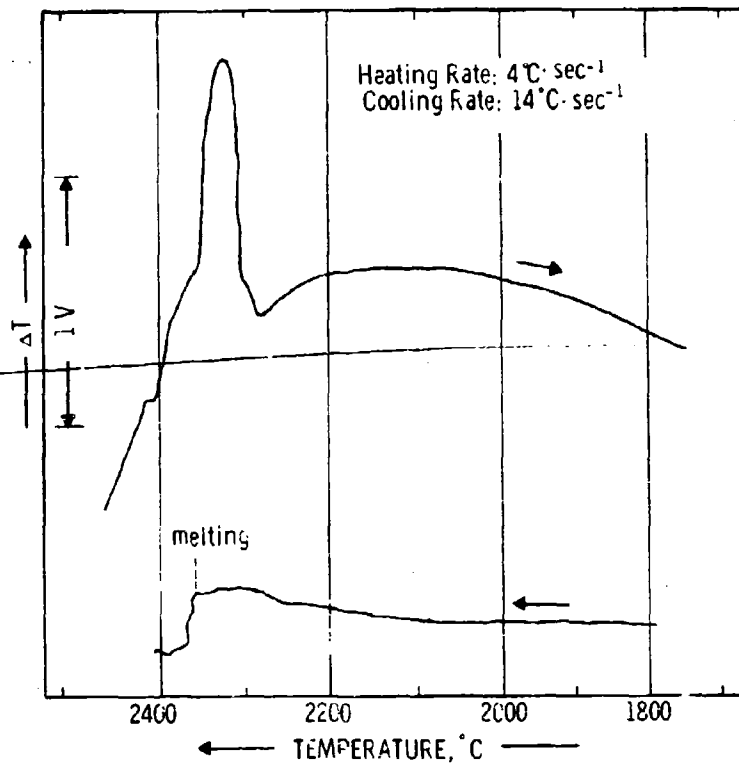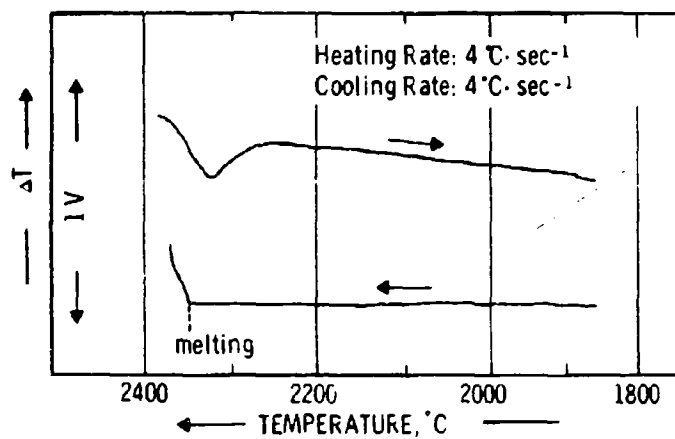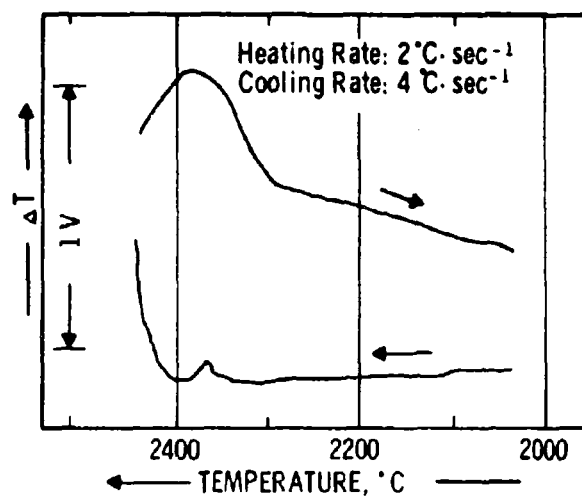
Figure 15. DTA-Thermogram of a Hf-C Alloy with
33 Atomic Percent Carbon.
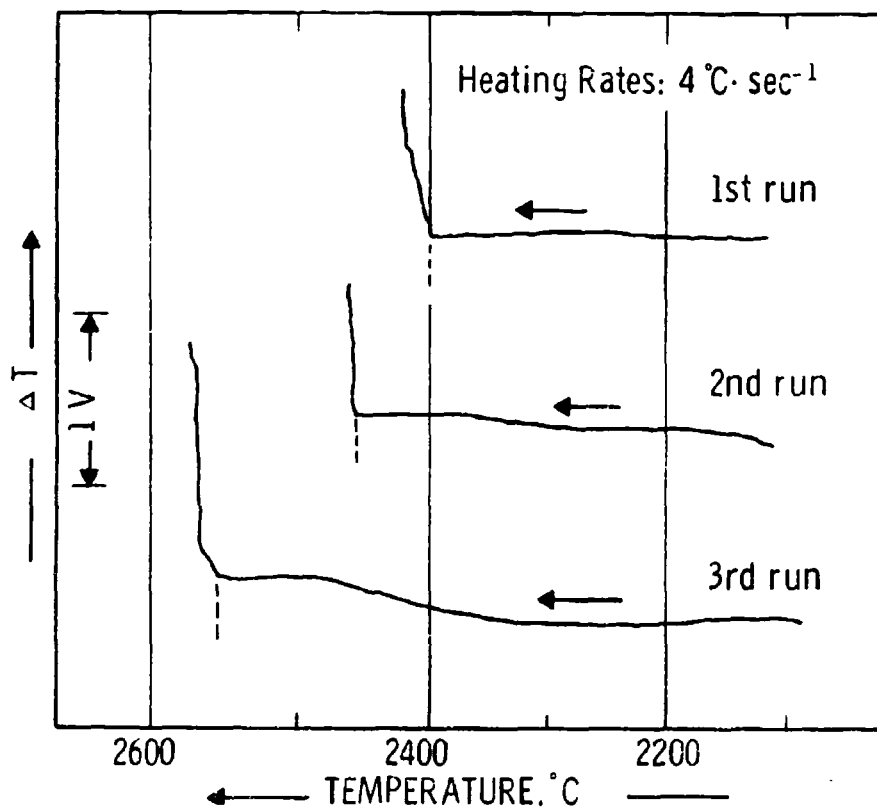
Figure 16. DTA-Thermograms (Heating) of a Hf-C Alloy
with 34 Atomic Percent Carbon .

(Carbon Content After 3rd Run: 34.7 At%)

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The results of the metallographic examination of metal-rich alloys are summarized in Figure 17, and are in general confirmation of the findings obtained by differential thermal analysis. Alloys equilibrated and quenched from above the peritectic line were two-phased, containing monocarbide and metal-rich melt (Figure 18a and 19d), whereas complete or partial dissolution of the monocarbide occurs upon reannealing of the alloys at temperatures below the peritectic (Figures 18b, 19b, 20b, and 20c).
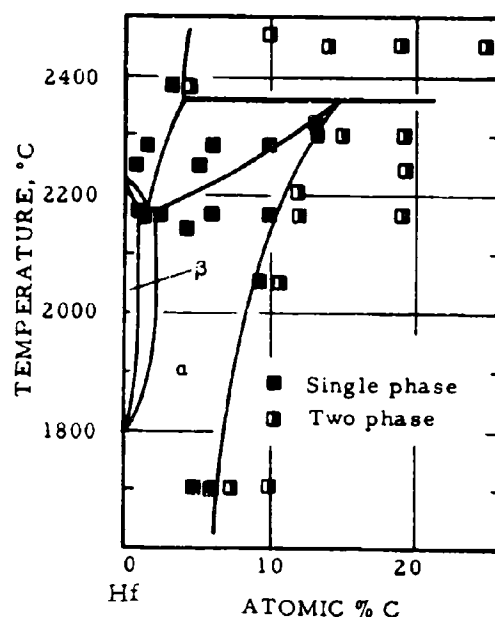
Figure 17. Metal-Rich Portion of the System Hafnium-Carbon: Qualitative Results of the Metallographic Examinations of Equilibrated and Quenched Alloys.
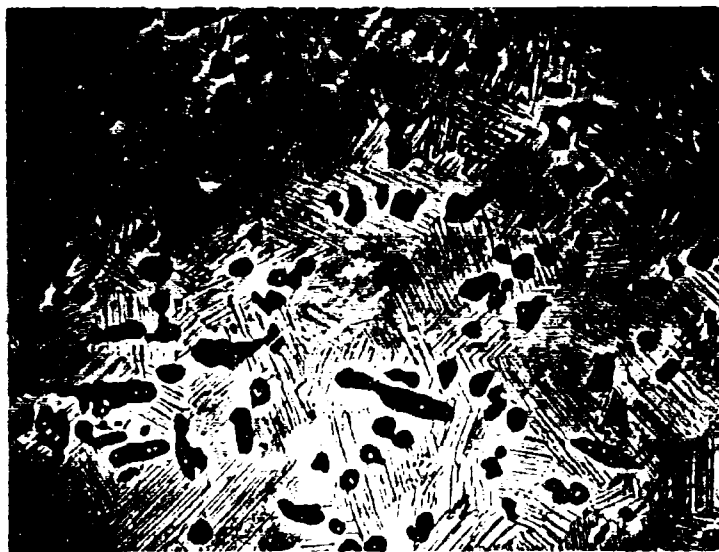
Figure 18a. Hf-C (7 At% C) Quenched from 2400°C.   X100

Monocarbide (Dark) in Matrix of α-Hf(Light
with Localized Precipitations of Monocarbide)

Figure 18b. Hf-C (7 At% C) Sample from Figure 18a,   X250

Re-equilibrated for 15 Minutes at 2150°C

(Slowly Cooled).

α-Hf-Solid Solution with Localized Precipitations of
Monocarbide.

29
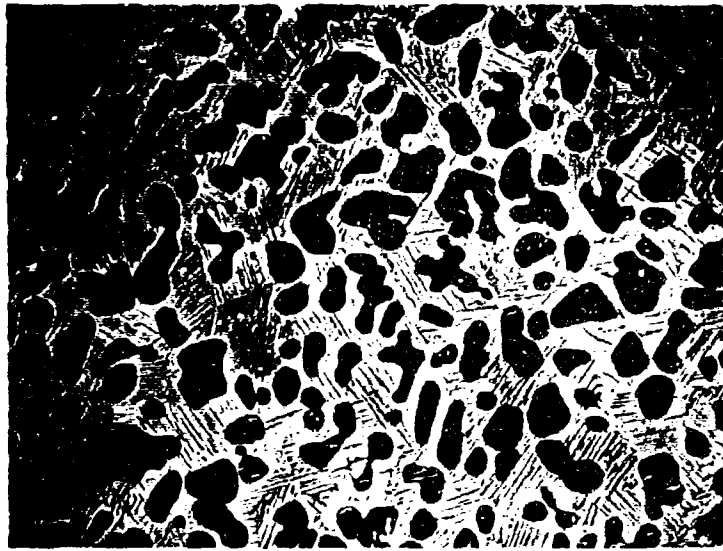
Figure 19a.   Hf-C (13 At% C), Quenched from 2450°C.   X100

Monocarbide (Dark, with Metal Precipitations), in a
Matrix of Metal-Rich Melt (α-Hf-ss with Carbide
Precipitations).

Figure 19b.   Hf-C (13 At% C) Sample from Figure 19a,   X150
Re-equilibrated at 2300°C and Quenched.

α-Hf-Solid Solution with Oriented Precipitation of
Monocarbide Formed During Cooling.

30

Precipitation of monocarbide from the α-Hf-solid solution occurs extremely fast and partial dissolutioning of the alloys upon cooling could not be prevented. Nevertheless, a differentiation between primary and secondary alloy constituents can be achieved fairly easily metallographically from the observed physical distribution of the phases after the equilibration and quenching treatments. The precipitation of the monocarbide occurs preferentially on selected crystal planes of the α-Hf-phase. (Presumably growth of the (111) plane of the cubic (B1) monocarbide phase on the $10\overline{1}0$ plane of the hexagonal close-packed α-Hf-phase)
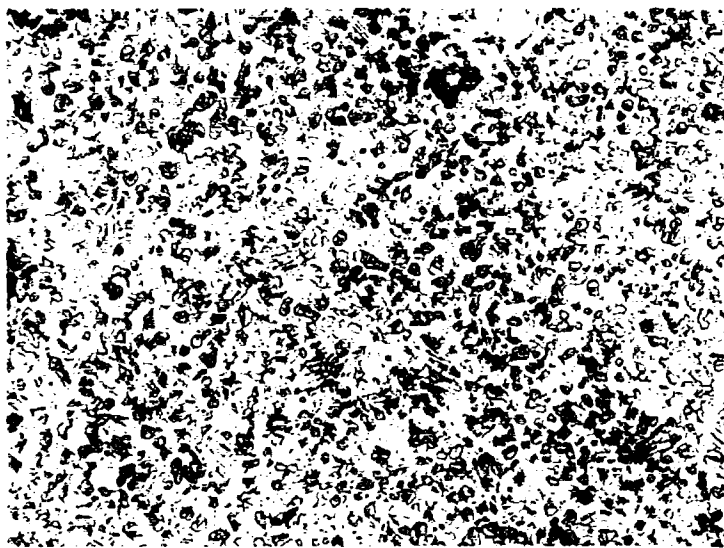
Figure 20a. Hf-C (14.9 At% C), Quenched from 2450°C.   X150

Monocarbide (Grey) in Matrix of Metal-Rich α-Hf
Solid Solution (Light Phase, with Precipitations of
Monocarbide)

Figure 20b   Hf-C (14.9 At% C).   Sample from Figure 20a   X450
Re-equilibrated for 15 Minutes at 2300°C.
Carbide Phase in Process of Dissolution

Figure 20c.   Hf-C (14.9 At% C) Sample from Figure 20a   X500
Re-equilibrated for 1 Hour at 2300°C.

α-Hf-Solid Solution with Oriented Precipitations of
Monocarbide Within the Grains and Small Amounts of
Excess Monocarbide Distributed Along the Grain
Boundaries.

While in alloys with total carbon concentration of up to 14 At% the dis-solutioning reaction proceeds to completion, i.e. the alloys are single phase α-Hf-ss upon heat-treatment slightly below the peritectic line, the appearance of small amounts of monocarbide as second phase was noticed in the alloy with 14.9 atomic percent (Figure 20c). The amount of excess monocarbide increases upon further addition of carbon (Figure 21 and 22). Based on the metallographic evidence, the homogeneity limit of the α-Hf-phase at the peritectic temperature was placed at 14 At% C.

X-ray examination was performed on all alloy material from this concentration range. Due to the rapid precipitation of monocarbide from the α-(Hf,C)-solid solution, the lattice parameter of the terminal solid solution at the peritectic temperature could not be deter-mined with certainty. The largest parameters, $a = 3.221$ Å, $c = 5.151$ Å, were obtained from an alloy with 25 At% C after rapid quenching (tin) from 2300°C. This is significantly higher than the parameters of the starting material ($a = 3.19_6$ Å, $c = 5.05_7$ Å), although post-quenching metallo-graphic examination showed, that considerable amounts of monocarbide had precipitated from the α-phase. Slower cooling (8 to 16°C·sec^{-1}) result-ed in alloys with parameters for the α-phase varying between $a = 3.202$ to 3.207 Å, and $c = 5.100$ to 5.107 Å.

The lattice expansion of the α-Hf-phase due incorpora-tion of carbon atoms is apparently much larger than in the corresponding system with oxygen[29], where the parameters at the homogeneity limit (20.5 At% O) are $a = 3.214$ Å and $c = 5.101$ Å, respectively.
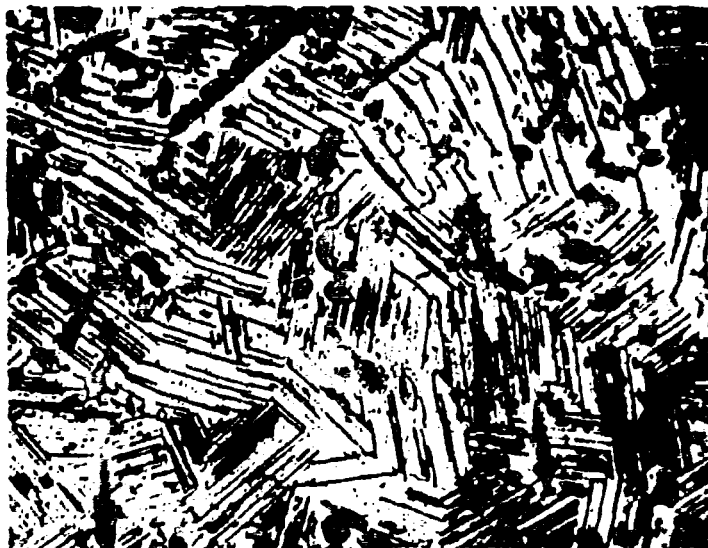
Figure 21.   Hf-C (16 At% C), Equilibrated at 2310°C, and   X500
Quenched.
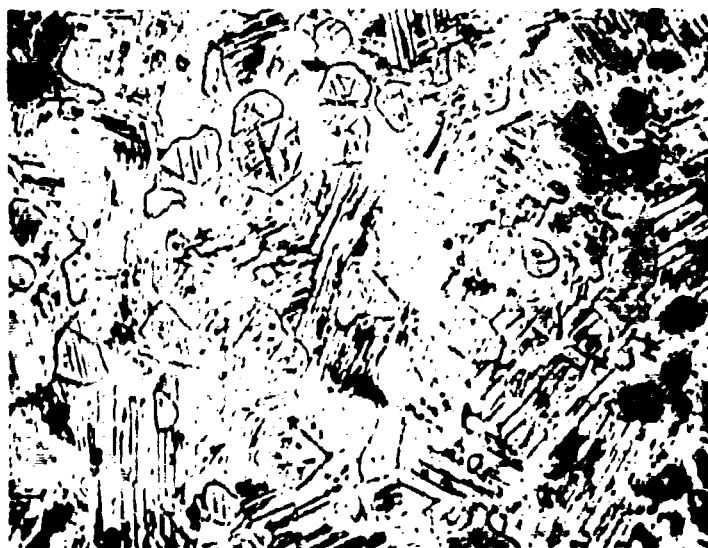
a-Hf-Solid Solution and Excess Monocarbide.

Figure 22.   Hf-C (19 At% C), Equilibrated at 2310°C, and   X500
Quenched.

a-Hf-Solid Solution with Monocarbide Precipitation,
and Monocarbide (Shaded, with Localized Metal Pre-
cipitations).

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Similarly as experienced with hafnium-oxygen alloys[29], the incorporation of carbon atoms into the hexagonal close-packed α-hafnium lattice causes a severe embrittlement and increase of hardness of the metal phase: Alloys with carbon concentrations higher than approximately 7 to 8 atomic percent can be crushed and powdered without any difficulty and apparent deformation of the parent lattice. At the low carbon concentration of the peritectic (∼ 5 At% C) the metal phase at this composition still exhibits a certain amount of ductility, and it was interesting to note, that two-phase (Hf + HfC) alloys, quenched from temperatures above 2360°C, were quite tough, while reannealing of the alloys at sub-peritectic temperatures resulted in brittle bodies (formation of the α-(Hf,C) solid solution).

Alloys with 25, 32.8, and 33.2 At% C are two-phased, consisting of monocarbide and metal (Figure 23a, 23b, and 23c), while an alloy with 34.3 At% C shows the monocarbide phase only (Figure 24).

5.   The Monocarbide Phase

The incipient melting temperatures of the alloys increase steeply as the carbon concentration is raised above 34 At% (Figure 16, Table 8). Congruent melting was observed at a carbon concentration of 48.5 At% and a temperature of 2438°C. Comparatively rapid precipitation of metal from the monocarbide phase was encountered up to total carbon concentrations of 37 atomic percent; at still higher concentrations quenching was not necessary to retain the metal in solution.

Metallographic examination of the alloys revealed homogeneity to compositions very close to stoichiometry (Figures 25 a through 25d). The average bound carbon content in alloys quenched in the

35
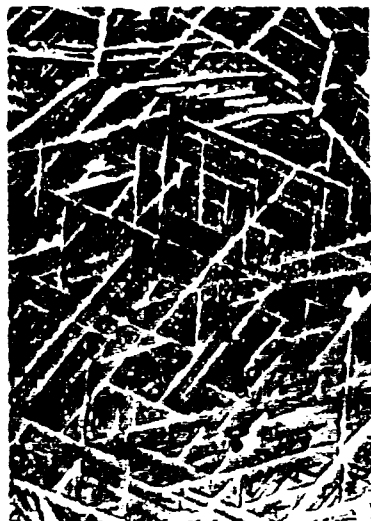
25 At% C	32.8 At% C	33.2 At% C
Quenched	Slowly Cooled	Quenched
(23a) X500	(23b) X500	(23c) X500

Figure 23. Micrographs of Hf-C Alloys Equilibrated at 2400°C
Structure Constituents: Monocarbide and α-Hf-Phase

Figure 24. Hf-C (34.3 At;. ,, Quenched from 24ΰ0°C.   X100
Single Phase Hafnium Monocarbide, and Pores (Black)
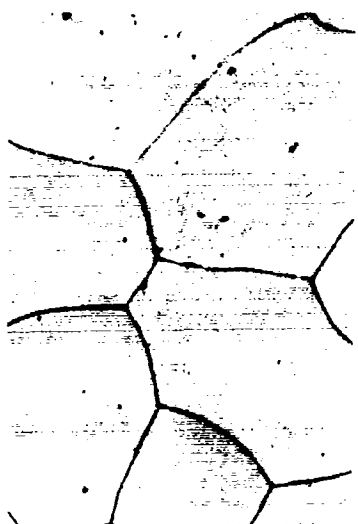
38.8 At% C, 3635°C ↓

Figure 25a   X200
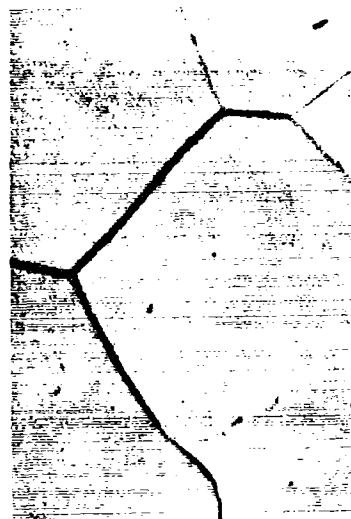
42.6 At% C, 3675°C ↓

Figure 25b   X500

temperature range from 2300 to 3800°C varied between 49.8 to 49.5 At%, i.e. the carbon-rich boundary over the entire temperature range is located very closely to 50 At% and retracts only at temperatures above 3800°C to 48.5 At%, the congruently melting composition. The lattice parameters of the monocarbide phase over the homogeneity range were determined on two alloy series, which were equilibrated at 1600°C, and 2260 - 2320°C, respectively (Figure 26), and show a nearly linear variation from a = 4.608 Å at ~34 At% C (4.619 Å at 38 At% C, the low carbon boundary at 1600°C), to a = 4.640 Å at the monocarbide-graphite boundary (49.5 to 49.8 At% C). It is interesting to note, that the largest parameter
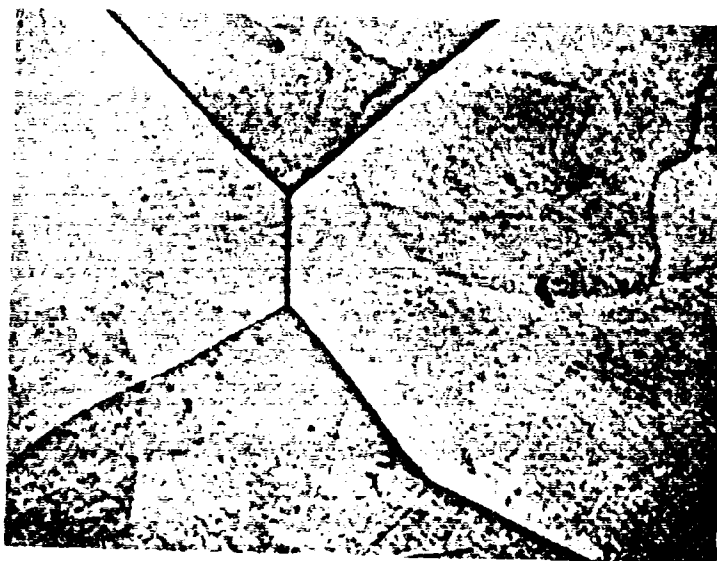
Figure 25 c.   47.2 At% C, 3896°C ↓   X1000
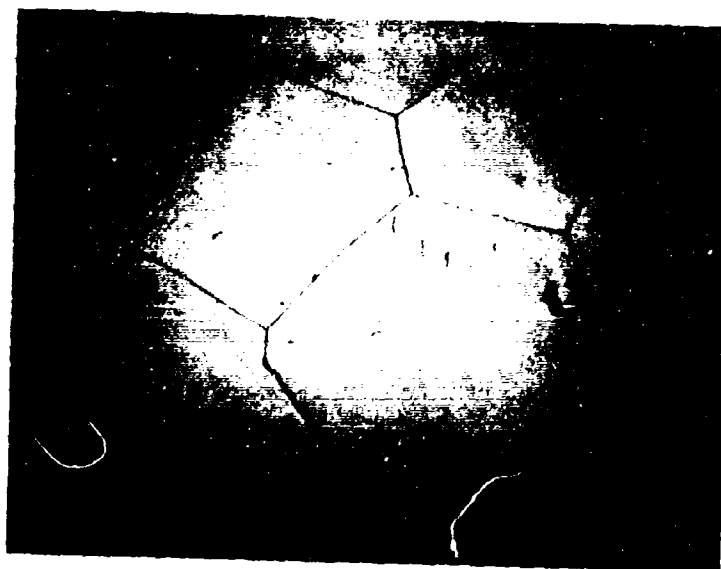
Figure 25d.   49 At% C, 3800°C ↓   X450

Figure 25 a - d: Single Phase Hafnium-Monocarbide Alloys

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a = 4.643 Å , was measured in alloys with an analyzed carbon content of approxi-
mately 49 At%, quenched from the molten state (3890°C). Excess carbon con-
taining alloys, quenched from temperatures above the Hf-C eutectic line, in-
variably showed smaller parameters (a = 4.637 to a = 4.639 Å). Apparently
the same phenomenon, whose origin is not yet fully understood, had been
observed by R.V. Sara and C.E. Lowell[28] on zirconium monocarbide; it is
thinkable, that partial interchanges between the metal and the semi-metal lat-
tice may take place at temperatures close to melting, or may occur as the result
of non-equilibrium crystallization, and are frozen-in in the quenching process.
The smaller parameters found for excess carbon containing alloys
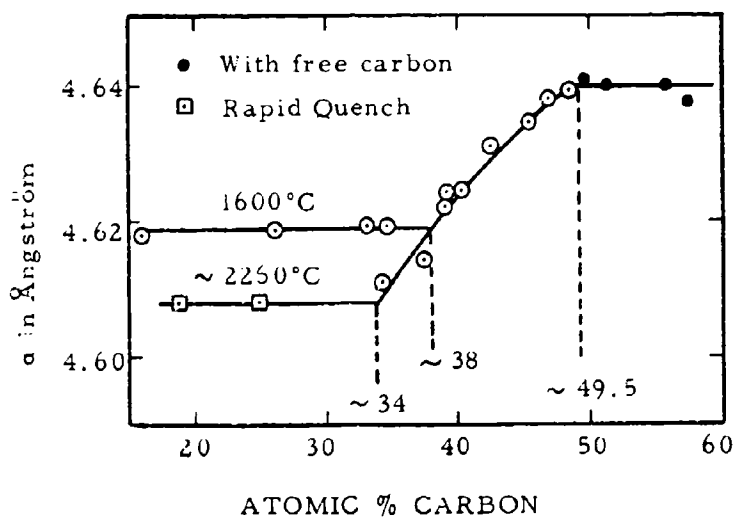
Figure 26. HfC$_{1-x}$: Variation of the Lattice Parameter
with the Carbon Concentration.
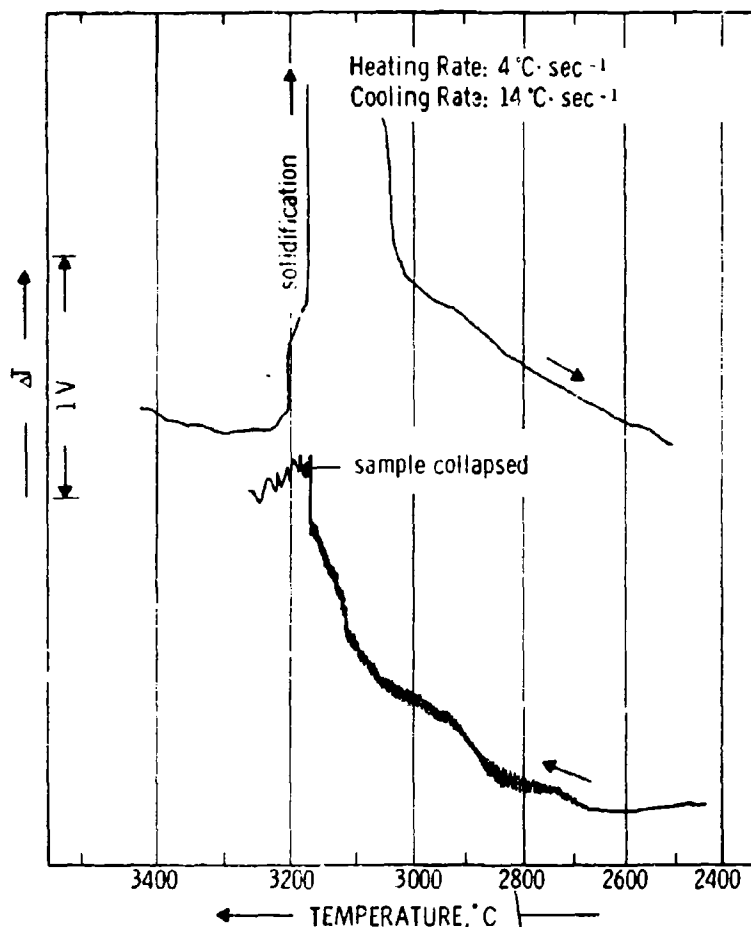
Figure 27. DTA-Thermogram of a Hafnium-Carbon Alloy
with 66 Atomic Percent Carbon.

(The gradual endotherm above 2800°C on the heating
cycle indicates higher vaporization rates (C + Hf) from
the porous test sample as compared to the graphite
reference sample).

would then be explainable by metal vacancies or carbon-occupied sites in

the metal parent lattice. In this connection, it is noteworthy, that the

lattice defects heal out upon annealing at lower temperatures, i.e. the
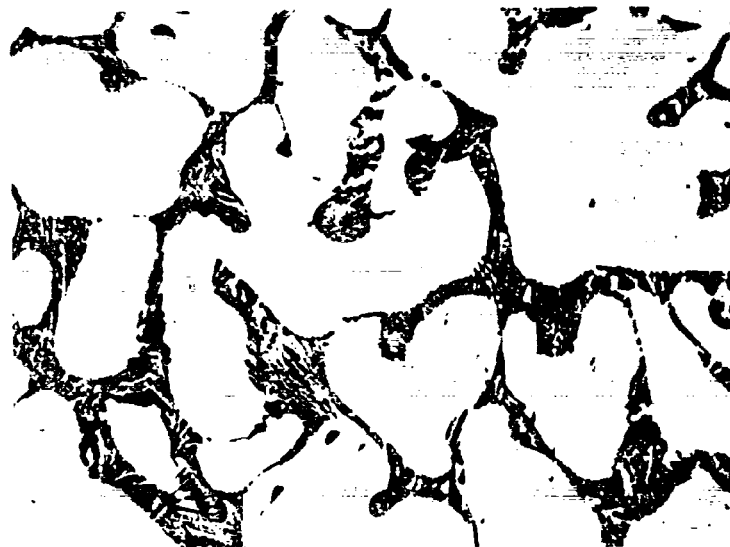
Figure 28a. Hf-C (56.1 At% C), Quenched from 3500°C.   X500
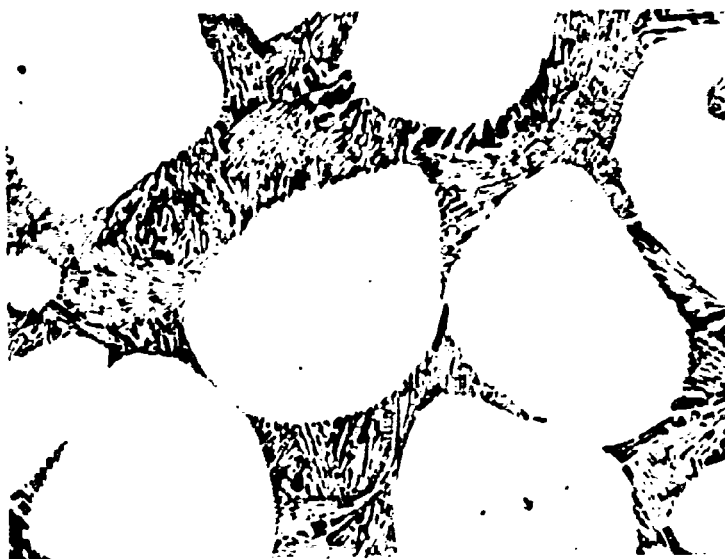
Figure 28b. Hf-C (38.5 At% C), Quenched from 3500°C.   X1000

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Figure 28c. Hf-C (60.3 At% C), Quenched from 3300°C.   X1000

Figure 28a - 28c: Hf-C Alloys from the Concentration Range 56 to 61 At% C,
               Quenched from Temperatures Above the Eutectic Line.

        Structure Constituents: Primary Crystallized Monocarbide
        in HfC + C Eutectic Matrix.

lattice parameters again resume the values exhibited by the lower tem-

perature equilibrated alloys.

        6.   The Concentration Range Monocarbide-Graphite

                Formation of liquid in alloys with carbon concen-

trations slightly above 50 atomic percent was difficult to observe, and noted

with certainty only at temperatures far in excess of the eutectic line

(Table 8, Figure 8). Melting occurred practically isothermally in the alloys

having carbon concentrations between 58.5 and 73 At% C. A eutectic
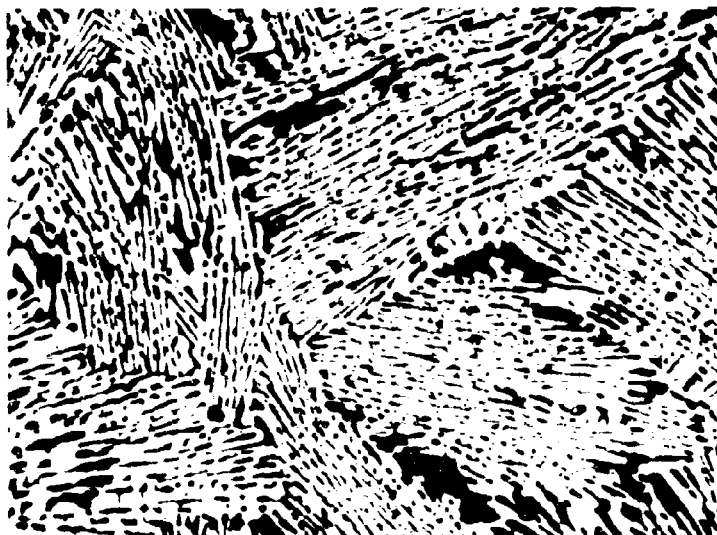
Figure 29.   Hf-C (65.2 At% C), Quenched from 3200°C.   X1000

HfC + C Eutectic

Figure 30.   Hf-C (73.2 At% C), Rapidly Cooled   X100

(~ 40°C sec) from 3400°C.

Primary Crystallized, Platelet-Shaped Graphite
in a Matrix of HfC + C Eutectic.

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Figure 31. Hf-C (82 At% C), Rapidly Cooled from 3700°C .   X100
Primary Graphite and HfC + C Eutectic

temperature of 3180°C was derived from the measurements (Table 8).
This result was independently confirmed by differential thermal analysis
(Figure 27).

Metallographic analysis showed alloys from the concen-
tration range 50 to 63 At% C to be two-phased, containing primary crystal-
lized monocarbide in a matrix of HfC-C eutectic (Figures 28 through 28c).

An alloy with an analyzed carbon content of
65.2 At% C was purely eutectic (Figure 29), and specimens with carbon con-
centrations above 66 At% C show increasing amounts of primary crystal-
lized graphite (in platelet-shaped form) in a eutectic matrix (Figures 30
and 31).

The results of the experimental investigations have

be en combined to develop the phase diagram shown in Figure 1.

IV.   DISCUSSION

The newly established phase diagram follows in its basic layout

the system presented by R. G. Avarbe, et.al.[18]. Our findings, however,

are more in favor of the existence of a eutectic reaction isotherm between

the α- and β-Hf solid solution, rather than a peritectic decomposition of

the β-phase, as suggested by these authors. Also, their temperature for the

peritectoid decomposition of the α-(Hf,C)-solid solution (2820°C, Figure 3)

is certainly too high. An explanation for these deviations may possibly be

sought in the extreme heterogeneous melting (compare the liquidus curve

in Figure 1) of the alloys in this concentration range, which makes the

direct pyrometric observation of incipient melting rather difficult. Oxygen

contamination as the possible error source, as suggested by R. V. Sara

and C. E. Lowell[8] is to be excluded, since the corresponding alloys are

lower-melting[29].

The metal-rich boundaries of the monocarbide are in good agree-

ment with previous determinations at the respective equilibrium tem-

peratures[8, 9, 10, 16, 18]. The carbon-rich phase boundary found by us is

in substantial agreement with the observations by R. V. Sara and C. E. Lowell.

It should be kept in mind, however, that the 49.5 At% C (2000 - 2500°C),

given by us refer to the firmly established lower limit. Analysis data on

a number of alloy specimens indicated bound carbon contents as high as

49.9 At%. These results, however, showed poor reproductibility, and

were therefore not considered in the final data evaluation.

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A comparison of the melting temperatures of the monocarbide phase reveals, that the measurements by C. Agte and H. Alterthum[14], made over 30 years ago, still appear as the most accurate to date, whereas, with the exception of the data by R. P. Adams and R. A. Beall[15] (Table 3), more recent investigations yielded values, which are too low[8, 16]. The most liekly error source will probably have to be sought in employing inadequate techniques for the measurements. Thus, one would suspect that rapid carbon exchange reactions, taking place between hafnium-carbon alloys and the tantalum carbide containers, used in the method by R.V. Sara and C. E. Lowell[8], may have changed the effective composition of the test samples and resulted in too low values.

Our determination of the eutectic point HfC + C, (65 At% C, 3180°C,) is in confirmation of the data by R. V. Sara and C.E. Lowell[8] (66 At% C, 3150°C), R. P. Adams and R. A. Beall[15] ($\sim$ 3220°C), K. I. Portnoi, et.al.[17] (3250 + 50°C). The value of 2915°C, determined by N. H. Krikorian[7] at the Los Alamos Scientific Laboratory, as well as the earlier reported temperature of 2800°C by Cotter and Cohn[5] for this reaction isotherm appear as somewhat low.

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The alloy system hafnium-carbon was investigated by means of X-ray, DTA, and melting point techniques on chemically analyzed alloys, and a complete phase diagram was established.

The results are discussed and compared with previously reported data.

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